DOI 10.1007/s10717-014-9658-2
Glass and Ceramics, Vol. 71, Nos. 7 – 8, November, 2014 (Russian Original, Nos. 7 – 8, July – August, 2014)

UDC 666.1 031

EFFECT OF THE REDOX POTENTIAL ON THE COOKING AND PROPERTIES OF GLASS

N. I. Min'ko[1, 2] and I. I. Morozova[1]

Translated from *Steklo i Keramika*, No. 7, pp. 8 – 11, July, 2014.

An analytical review of the literature on changes in glassmaking processes, diathermancy of molten glass and light transmission of glass as a function of the redox potential of the raw material and batch is given. Experimental data on the effect of the redox potentials (RP) of batches and cullet on the color of glasses with commercial compositions are presented. The conditions for transformations and equilibrium of iron oxides in glassmaking are examined.

Key words: glass, equilibrium oxide forms of iron, batch, glassmaking, chemical oxygen demand, redox potential.

The redox potential (RP) of raw material and batch affects the redox conditions of glassmaking, which in turn not only determines the color of glass but also the glassmaking and glass formation process itself. Instability of the redox conditions of glassmaking changes the diathermancy of molten glass, degrades the uniformity and quality of glass not only with respect to light transmission but also the appearance of technological flaws. For this reason, to secure the redox conditions of glassmaking it is necessary to monitor the RP of the raw materials and batch closely and to adjust the composition of the batch and glassmaking processes as needed.

Special interest in this question arose in Russia over the last decade. The first foreign works on the RP appeared in 1978 (W. Simpson, D. Myers, W. Marning, R. Davis, H. P. Williams, et al.). Work in this direction is continuing, and an oxygen sensor for determining the redox state of glass melt has been developed, for example, by the German company Kuhreich & Meixner.

In our country Yu. A. Guloyan and his colleagues began work on the RP in 1985, and N. A. Pankova [1] and her colleagues and graduate students in the department of glass at the D. I. Mendeleev Russian Chemical Technology University have been working in this field since 1990 [1]. The first works of the department of glass at BGTU on determining the RP were published in 1993 [2, 3]. The department devotes special attention to RP questions in preparing students and in courses on improving the skills of specialists in glass plants. The department's staff is also determining the RP for production plants as part of contract work.

Today, the RP of raw materials and batch in glassmaking is a pressing issue. Many plants have instituted such control. Scientific investigations in this direction are continuing. In addition to the authors' and schools mentioned above, the following work should be mentioned: V. I. Kiyan and A. B. Atkarskaya on sheet glass (Avtosteklo plant), V. A. Fedorova (town of Gus'-Khrustal'nyi) on high-quality glass, I. N. Gorina and G. A. Polkan (Saratov Scientific-Research Institute of Glass) on decorative materials, N. S. Krashennikova, V. I. Vereshchagin, et al. (Tomsk Polytechnic University) on new forms of raw materials, L. A. Korshunov (Scientific and Industrial Association Tsentr-Steklo-Gas) on container glass, V. D. Tokarev, V. I. Litvin, et al. (Salavatsteklo) on float glass and A. P. Sivko on illuminating glass. The method of determining the RP has been adopted in many plants.

An important parameter that is by no means always taken into account in sheet and container glass technology is the ratio of the oxide forms of 3*d* elements, especially iron, which, in spite of the enrichment methods used, is an attendant impurity in sand, dolomite, feldspar and other raw materials.

No less important in recent years is the presence of chromium and sulfur in glass and the ratio of their oxide forms, which can also be present in the raw material or be used as colorants [4].

[1] V. G. Shukhov Belgorod State Technological University (BGTU), Belgorod, Russia.
[2] E-mail: minjko_n_i@mail.ru.

The content (by weight) of iron oxides is comparatively low in commercial sheet glass (up to 0.15%) and up to 1% in heat-resisting glass. For domestic raw material the iron content in glass is as follows (wt.%): for crystal 0.025 – 0.04, decolored high-quality glass 0.04 – 0.07 and decolored container glass 0.05 – 0.9. These data are practically a factor of two or three greater than the iron content in glass produced by the best foreign companies.

The change in the light transmission of so-called colorless glass and the disruption of the stability of the technological process are due to the total iron content, especially the ratio of Fe(II) and Fe(III), i.e., the state of the equilibrium Fe(II) $\leftrightarrow$ Fe(III), which fluctuates within wide limits. The fluctuations of the total content of iron oxides in sheet glass even with no change in the raw materials can range from 0.05 to 0.15% in the course of one month. In addition, some plants are striving to switch to local sands with higher iron content. The methods of stabilizing the content of iron oxides are well known [5]: determining the upper limit of the content of iron oxides in glass on the basis of statistical data on the operation of the system and subsequent introduction of an iron-containing component into the batch taking account of its content in the raw materials for iron oxide content deviations in glass deviating 0.01%.

Iron in the form Fe(II) is decisive for the glassmaking process and, correspondingly, the technical and economic performance of furnaces. It lowers the diathermancy of the molten glass as a result of absorption at $\lambda = 1100$ nm and worsens the penetration of IR radiation into the interior of the molten glass.

Bivalent iron lowers the total light transmission of glass as a result of the appearance of light blue color, which is 10 – 15 times more intense than in the case of yellow-green color due to trivalent iron at the same concentration. Yellow color can appear in combination with sulfur in the form of sulfide as a result of absorption in the range 500 – 575 nm.

It is no less important to monitor the shift of the equilibrium in the Fe(III) direction, since in this case the layers of molten glass at the bottom are heated through and are drawn into the production flow, which is often the reason for the appearance of bubbles, stones and striae in the glass. The methods of shifting the equilibrium Fe(II) $\leftrightarrow$ Fe(III) rightward form the basis of the chemical method of decoloring glass. Sulfates play a significant role for glasses produced in large-tonnage amounts [6].

A stationary layer of molten glass is always present at the bottom of every glassmaking furnace with temperature of about 1300 – 1400 °C without additional electric heating (AEH). Oxygen from the furnace gases has practically no access to this layer because the diffusion coefficients are small [7]. The bottom layers are enriched with a reducing form of iron, as a result of which the chemical composition is different from that of the main mass of the glass. For this reason, the appearance of such molten glass in the production outflow with increasing diathermancy of the molten glass shifts the gas equilibrium in the glass and can result in the appearance of gaseous inclusions.

In summary, the content of iron oxides and unstable ratio Fe(II) $\leftrightarrow$ Fe(III) shifting in one or the other direction adversely affects the glassmaking process, giving rise not only to flaws but also chemical and thermal nonuniformity of the glass, which in turn lowers the strength, heat resistance and chemical stability of the glass and results in a large amount of cullet and defective glass.

The diathermancy of molten glass, especially radiant thermal conductivity, determines the regime required for forming glass articles by a mechanical method. Increasing the Fe_2O_3 mass fraction even from 0.03 to 0.16% and FeO from 0.01 to 0.04% lowers the thermal conductivity 5.5-fold. Increasing the content of iron oxides in green container glass in the presence of Cr_2O_3 reduces the radiant thermal conductivity 30 – 35-fold [8]. For this reason, when the redox conditions of glassmaking change, the thermal conductivity changes by an order of magnitude, which can make the formation process unstable. Increasing the iron content in glass, especially Fe(II), can lower the temperature of the molten glass at pouring and give rise to crystallization of the glass. In addition, the formation interval of the more intensely colored glasses, including those colored by Fe(II), is shorter.

The following factors influence the shift of the equilibrium Fe(II) $\leftrightarrow$ Fe(III):

– RP of the raw materials and batch;
– moisture content of the batch;
– total iron oxide content in the batch and glass;
– presence of oxidizers and reducers in the batch;
– acid-base properties of the glass composition;
– temperature-time regime of glassmaking;
– gas regime of glassmaking, the redox conditions;
– extraction of the molten glass;
– presence together with iron of other 3*d* and 4*f* elements, i.e., elements whose oxidation state can change, in the batch and molten glass.

The most acceptable method of determining the RP of raw material and batch is analytical determination of the chemical oxygen demand (COD), i.e., the amount of oxygen required to oxidize the reducers and impurities in the raw material and batch. The COD is determined experimentally by means of bichromatometry or permanganometry. The RP is calculated according to the carbon number based on the redox reactions in the batch. The batch recipe must be adjusted on the basis of the COD data for each composition of the batch, the quality of the raw materials and specifically for every glassmaking furnace and its operating regime.

We investigated the effect of the RP of the batches (from +168.5 to –121.1) for standard glass compositions on the glassmaking process and quality of the glass [3]. Glasses with different color were obtained: from yellow-green $\to$ green $\to$ blue-green to yellow-brown and black, owing to the coloration method in the system Na_2SO_4–C–Fe_2O_3. For strongly oxidizing potentials (RP > +120) the iron in the

glass is in form Fe(III), giving rise to weak yellow-green color of the glass. For RP from –20 to +120 the iron in the glass is in the two forms Fe(II) and Fe(III) and a superposition of the light-blue and yellow colors is observed, which gives different shades of green. For reducing potentials (RP from –20 to –120) the equilibrium shifts in the Fe(II) direction, giving a blue color, while in the presence of Fe(III) a blue-green coloration characteristic for heat-shielding glass obtains [9].

In compositions with high carbon content the colors ranging from brown to black are due to the appearance of sulfide sulfur S^{2-} in the melt, where in this case the colorant is an iron oxide – sulfide chromophore. The amber color of the glass is obtained from batch with RP from –20 to –60. It is obvious that the value of the RP of the batch and the corresponding color of the glass depend on the temperature-time and gas regimes of glassmaking and will be individual for each industrial production system.

The RP of the raw materials varies over wide limits: sand 70 – 250, nepheline concentrate 60 – 85, limestone 35 – 70, sodium sulfate 20 – 35 and synthetic sodium sulfate 480 – 680. For example, when sand with RP = 99 is replaced by sand with RP = 155 the amount of carbon in the batch must be reduced by a factor of 2 in order to maintain the RP of the batch at the previous level. The moisture content of the batch also affects the value of the RP [10].

The RP of cullet must also be determined. According to our data it lies in the range 100 – 115, and the RP of aluminum and silver mirror cullet lies in the range 125 – 152. Our copious data on the RP fall within these limits. The introduction into molten glass (which is cooked under oxidizing conditions, for example, with oxidizers) of cullet made under reducing conditions can lead to the appearance of bubbles because of the solubilities of SO_2 and SO_3 in oxidized and reduced glasses are different. The correctness of adjusting the batch should be determined according to the different contents of Fe(II) and Fe(III) in the glass (such methods are available) as well as according to the spectral characteristics of the glass, specifically in terms of the diathermancy index (DI), numerically equal to

$$\mathrm{DI} = 10^{-1} t_{1100},$$

where t_{1100} is the light transmission (%) of a 10 mm thick glass sample of glass at wavelength 1100 mm [11].

Such control and adjustment of the batch recipes make it possible to adjust the glassmaking regime (the effect of which is already seen in the warming up of the batch), stabilize the cooking conditions and, correspondingly, the glass quality and yield.

All other parameters making it possible to shift the equilibrium Fe(II) $\leftrightarrow$ Fe(III) and, correspondingly, the stability of the glassmaking process can be discussed only briefly here. The effect of each one can be determined with all others remaining stable, i.e., all other conditions being equal.

The equilibrium shifts in the Fe(II) direction with increasing total iron in the glass. Increasing the cooking temperature and time gives the same effect. The Fe(III) fraction increases with increasing basicity of the glass (the ratio of the amount of alkali and alkaline earth oxides to (SiO_2 + Al_2O_3), another glass former). In addition, even small changes in the chemical composition of the glass, the introduction of accelerators or other auxiliary raw materials of a basic or acidic character, correspondingly shift the equilibrium Fe(II) $\leftrightarrow$ Fe(III) in one or the other direction. For example, Na_2SiF_6 introduced to accelerate the cooking process is acidic [12].

In addition, it should be noted that the methods of analyzing the content of not only iron in glass but also the main components in the glass composition are important because the determination accuracy depends on the method used, the quality of the reagents and the equipment, as well as the subjective errors [13]. There are no standards for x-ray-fluorographic express-analyses of the elemental composition of glass in modern equipment.

The gas regime is regulated by feeding excess air. The transition to oxygen combustion of fuel, as has already been done abroad, requires additional research. As the total iron content in sand and other raw materials and, correspondingly, in the glass itself increases, its density of the glass increases, the light transmission decreases and the temperature of the bottom layers increases, the gradient of the velocities of the surface flows increases, and the batch-foam interface becomes unstable, which makes it necessary to increase the amount of gas fed to the burners in the cooking part. It has been suggested that the fuel flow rate to the burners as a function of the iron content in the glass be adjusted. This will make it possible to decrease the temperature nonuniformity of the molten glass in separate zones of the furnace and improve the quality of the glass.

The extractions of molten glass have now increased considerably simultaneously with an increase in the cooking temperature. According to the data in [14], from 1920 to 1989 the cooking temperature in the container glass furnaces increased from 1370 to 1600°C, while the specific extraction of molten glass has increased from 0.6 to 3.2 tons/m^2/day. But, most importantly, the stability of the extractions has also increased.

Other elements present in glass, which together with iron change the oxidation state, are oxidizers, colorants, decolorizers and reducers as well as impurities in the raw materials. Their effect on the shift of the equilibrium Fe(II) $\leftrightarrow$ Fe(III) should be examined by comparing the electrochemical potentials. The COD of the raw materials and batch also takes account of the presence of such components in the batch. It should be noted that the SO_3 content in glass can be regarded as a measure of the degree of oxidation of the molten glass [6].

In summary, control and taking account of the RP of raw materials, which can change even in the process of drying,

the use of unconventional forms of raw material [15], as well as control of the RP of the batch will make the glassmaking process more stable, which is directly related with high product quality.

REFERENCES

1. N. G. Lipin, L. A. Orlova, and N. A. Pankova, "Estimation of the redox potentials of glass batches," *Steklo Keram.*, No. 11 – 12, 12 – 13 (1993); N. G. Lipin, L. A. Orlova, and N. A. Pankova, "Estimation of the redox potentials of glass batches," *Glass Ceram.*, **50**(11 – 12), 464 – 466 (1993).
2. N. I. Min'ko, R. L. Bilinskii, and S. P. Bilinskaya, "Silicomanganese slag as colorant for silicate glasses based on sulfate and soda-sulfate mixtures with cullet," *Steklo Keram.*, No. 5, 2 – 4 (1993); N. I. Min'ko, R. L. Bilinskii, and S. P. Bilinskaya, "Silicomanganese slag as colorant for silicate glasses based on sulfate and soda-sulfate mixtures with cullet," *Glass Ceram.*, **50**(5), 187 – 190 (1993).
3. N. F. Zhernovaya, N. I. Min'ko, V. I. Onishchuk, and L. I. Mel'nikova, "The effect of the redox potentials of the glass batch and cullet on the color of commercial glass containing iron oxides," *Steklo Keram*., No. 3, 11 – 13 (2000); N. F. Zhernovaya, N. I. Min'ko, V. I. Onishchuk, and L. I. Mel'nikova, "The effect of the redox potentials of the glass batch and cullet on the dye of commercial glass containing iron oxides," *Glass Ceram*., **57**(3 – 4), 84 (2000).
4. Yu. A. Guloyan, "Investigation of the transformations of the coloring compounds in commercial-glass batches," in: *Collected Scientific Works on Investigations of Chemically Stable Glasses, Fibers and Materials based on Them* [in Russian], GIS, Moscow (1985), pp. 116 – 124.
5. N. A. Pankova, L. Ya. Levitin, I. V. Aleksandrova, and I. N. Gorina, "Methods of stabilizing the content of iron oxides in a glass composition," *Steklo Keram.*, No. 1, 4 – 5 (1980); N. A. Pankova, L. Ya. Levitin, I. V. Aleksandrova, and I. N. Gorina, "Methods of stabilizing the content of iron oxides in a glass composition," *Glass Ceram.*, **37**(1), 3 – 6 (1980).
6. N. I. Min'ko and I. M. Binaliev, "Role of sodium sulfate in glass technology," *Glass Ceram*., No. 11, 3 – 8 (2012); N. I. Min'ko and I. M. Binaliev, "Role of sodium sulfate in glass technology," *Glass Ceram*., **69**(11 – 12), 361 – 365 (2013).
7. Yu. A. Guloyan, "Conditions for the transformations and equilibria of iron oxides in glassmaking," *Steklo Keram*., No. 1, 3 – 5 (2004); Yu. A. Guloyan, "Conditions for transformation and equilibrium of iron oxides in glass melting," *Glass Ceram*., **61**(1 – 2), 3 – 5 (2004).
8. Ya. D. Konovalova and L. R. Yurkov, "On some thermophysical properties of container glasses," *Steklyannaya Tara*, No. 9, 8 – 9 (2003).
9. N. I. Min'ko, A. B. Atkarskaya, A. A. Myagkaya, and I. V. Tret'yakov, "Stabilization of glass spectral characteristics and technology," *Steklo Keram*., No. 3, 18 – 21 (2011); N. I. Min'ko, A. B. Atkarskaya, A. A. Myagkaya, and I. V. Tret'yakov, "Stabilization of glass spectral characteristics and technology," *Glass Ceram*., **68**(3 – 4), 87 – 90 (2011).
10. G. A. Polkan, N. I. Gorina, and V. T. Matorina, "Investigation of the effect of batch preparation, loading and temperature-time conditions on the opacifying properties of 'Dekorit' glass," in: *Reports at the 1st International Conference Glass Progress 21* [in Russian], Saratov (2002).
11. A. B. Atkarskaya and V. I. Kiyan, "The reasons for change in heat transparency of the glass melt in an operating tank furnace," *Steklo Keram*., No. 10, 8 – 10 (2001); A. B. Atkarskaya and V. I. Kiyan, "The reasons for change in heat transparency of the glass melt in an operating tank furnace," *Glass Ceram*., **58**(9 – 10), 335 – 337 (2001).
12. P. A. Bingham, I. M. Parker, T. Searle, I. M. Williams, and I. Smith, "Novel structural behaviour of iron in alkali-alkaline earth silica glasses," in: *International Congress on Glass, Vol. 2, Edinburgh, 1 – 6 Julie, 2001*, Edinburgh (2001), pp. 202 – 203.
13. S. G. Sushkova and E. A Didenko, "State of chemical control of the composition of glass at enterprises in the industry," in: *Collection of Scientific Works of the State Institute of Glass on the Chemistry and Technology of Glass* [in Russian], Moscow (1983), pp. 9 – 13.
14. Zh. I. Dzhao-Rakitin and G. Takel's, *Electrically Fused Refractories and Modern Glassmaking Furnaces* [Russian translation], Sorg Company (1989).
15. N. I. Min'ko and I. I. Morozova, "Use of secondary and unconditioned raw material in the technology of construction glass materials," in: *Scientific and Engineering Problems of Construction-Technological Utilization of Technogenic Wastes* [in Russian], V. G. Shukhov State Technological University, Belgorod (2014), pp. 42 – 49.